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Civil and Environmental Engineering

Trash-to-(Fly Ash)-to-Treasure: Lessons learned from coal combustion residuals and their applicability to WTE-derived residuals (ashes)

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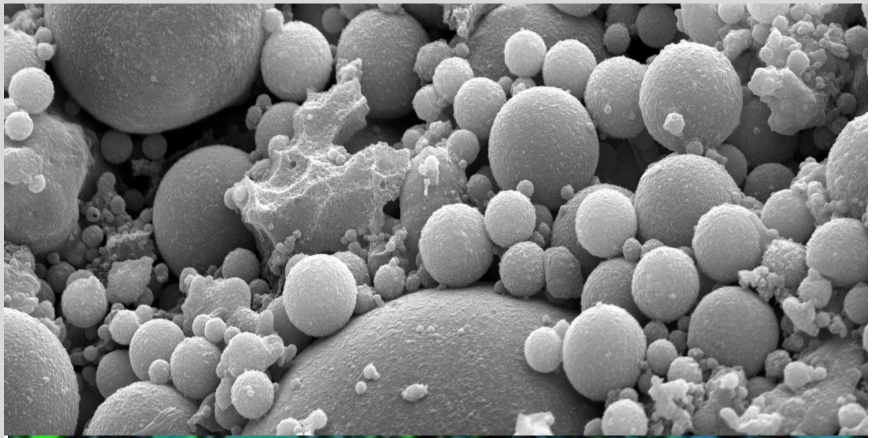
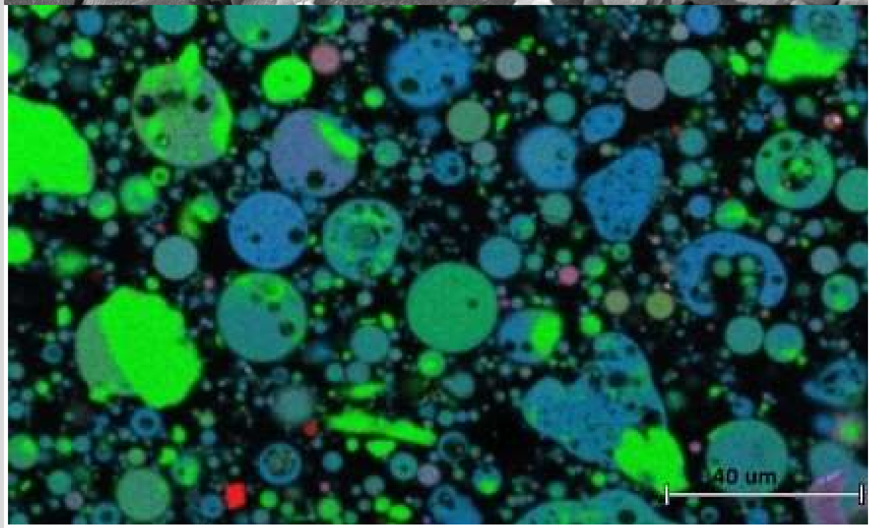
Presentation outline

- Complexities of fly ashes (coal combustion residuals)
- Fly ash’s behavior is a function of glass connectivity
- Chemical compositions and rigidity of atomic networks
- Linking network rigidity and dissolution rates (i.e., reactivity and durability) within a common framework
- Summary and conclusions

What is fly ash and why it is so complex ?

- Residual of coal combustion process
- Two flavors of fly ash: Ca-rich (Class C) and Ca-poor (Class F); as function of the parent coal composition
- Fly ash is widely used to replace OPC (cement) in concrete
- Fly ashes show wide variation in their composition (figure alongside)
- Fly ash also varies across geographic locations, and across seasons
- Frequent characterization is needed





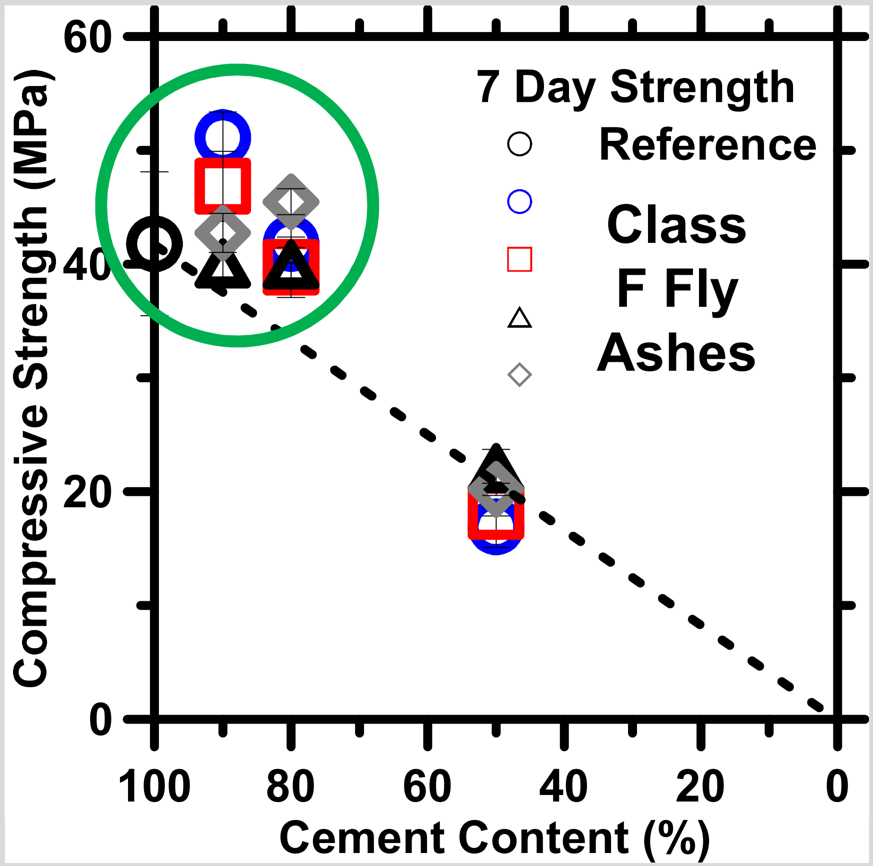
Selecting the optimal fly ash to replace OPC ?

- Often, it is desired to replace OPC using SCMs such as: fly ash, calcined clays, slags, etc.
- All of these materials are known to be “less reactive” than OPC
- There is no rapid means to link composition to reactivity and assess: (i) Suitability (dosage) for OPC replacement, (ii) Rapidly select one fly ash over another

Choices (fly ash) and Consequences (properties) ?

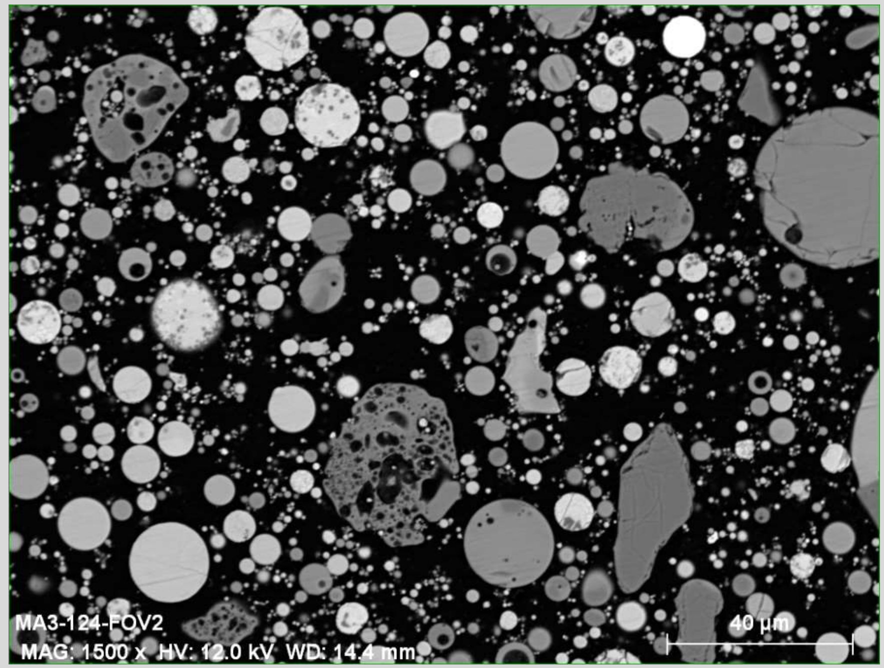
Other aspects to be considered for fly ashes ?

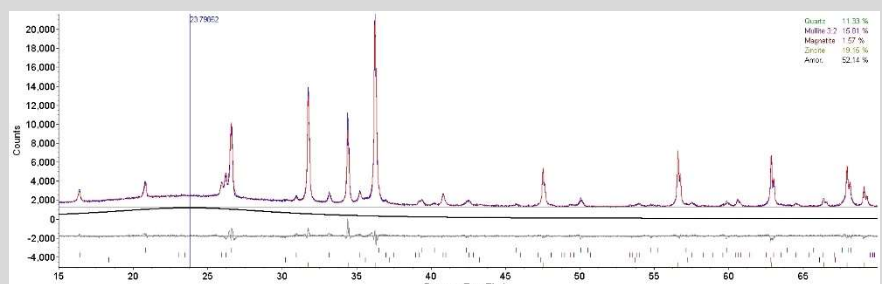
- Current standards answer the question of compliance (Class C or Class F), but not performance
- So, is there a way to assess the reactivity of the glass in fly ash and link it to its composition and structural features ?
- Focus on the glassy compounds as they are dominant, e.g., they often make up > 65 mass % in typical (commercial) fly ashes



Fly ash reactivity: Assessing glass composition

- Seven commercial U.S. fly ashes that span both Class C and Class F designations
- Fly ashes were characterized in terms of particle size, and their compositions using:
  - XRF (simple oxide composition)
  - XRD (mineralogy)
  - SEM-EDS (composition mapping)
- Average glass composition ascertained from XRF and XRD

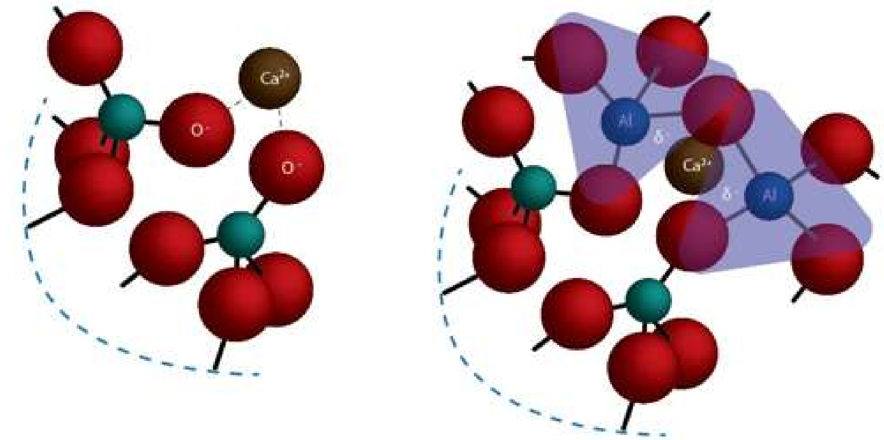




Suitability of a fly ash for OPC replacement ?

Glass Properties Depend on How "Connected" Its Atoms Are

- The structure of glass is a network
- As composition varies, glass networks become either more or less connected
  - "Modifiers" like calcium (Ca) produce disconnections in structure
  - Other elements like aluminum (Al) can result in more connections
- In other contexts, "connectivity" is related to glass properties, e.g., reactivity as is relevant for fly ash



Our goals: (1) Identify fly ash attributes that affect concrete performance, and (2) Offer simple methods for ease of use

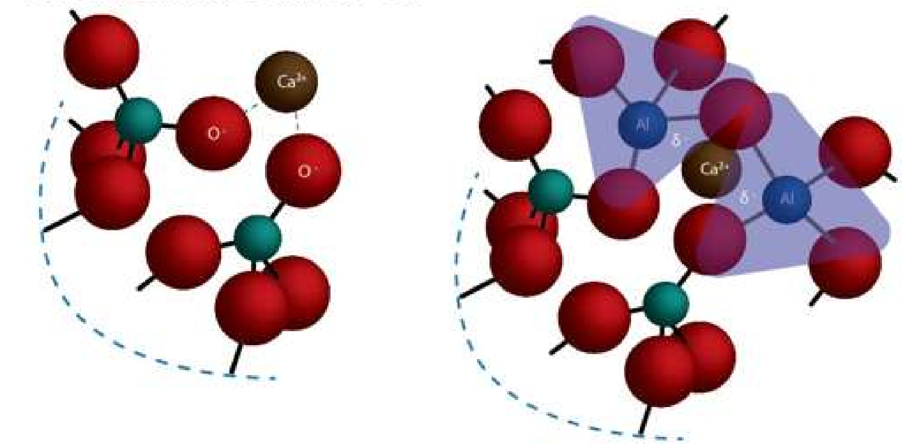
Relating structure-composition-performance

"Connectedness" can be calculated from chemical composition

- The average number of disconnects per structural unit was calculated for fly ash
- This accounted for overall influence of composition (e.g., Ca, Al, etc.) on the fly ash's glass structure
- This metric was called network ratio, as it is similar to a ratio between elements that make fly ash more (Ca) or less (Al) reactive, respectively

Silica Glass + Network Modifier Ca

Silica Glass + Network Former Al

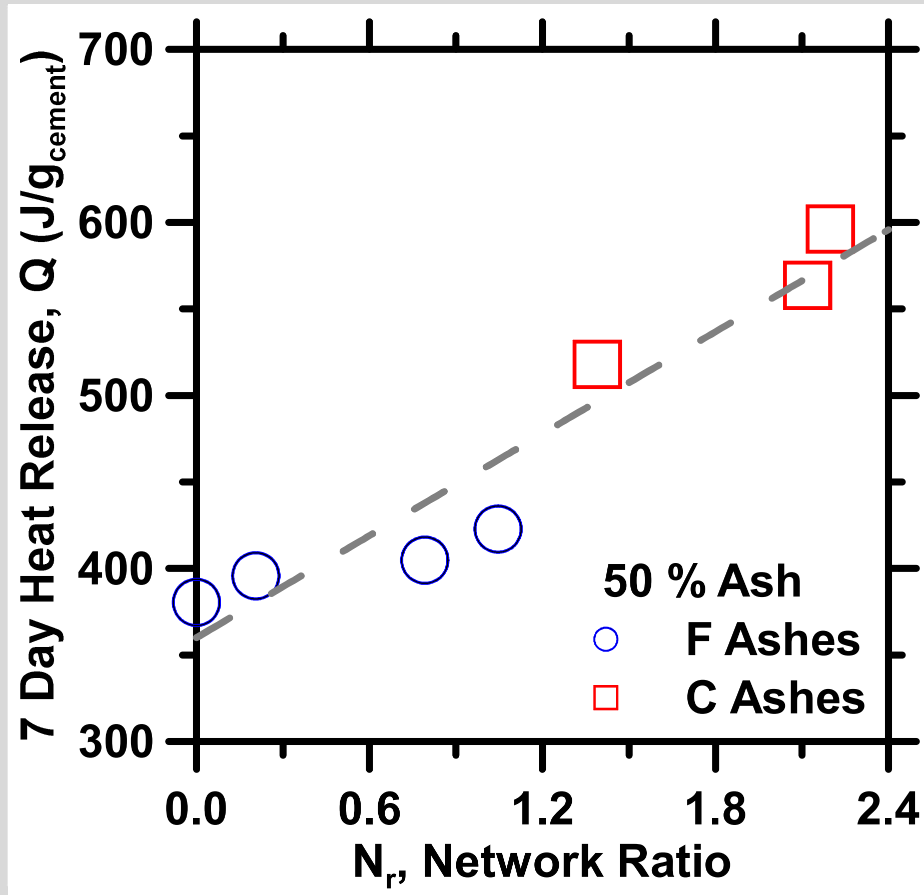


$$N_r = \frac{2 \times (X_{Ca} + X_{Mg}) + X_K + X_{Na} - X_{Al}}{X_{Si} + X_{Al}}$$

The relevant question: This looks simple but does it work ?

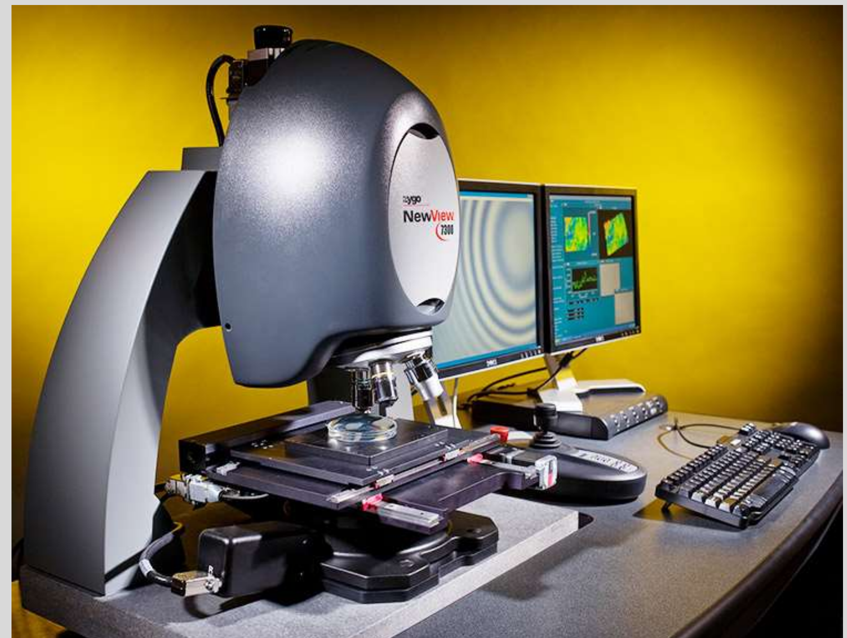
Relating network ratio (N_r) to performance

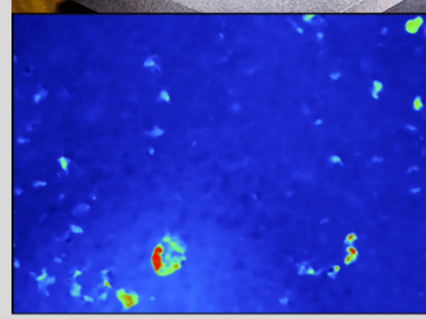
- Network ratio (N_r) is physically meaningful and shows range of differences for fly ashes across the Class C, Class F designations
- **Advance:** It is related to higher order measure-ables including density, and diffuse-peak position
- **Advance:** It is correlated with reactivity (heat release behavior) and engineering performance (strength) descriptors
- Offers a basis to rank, order and select fly ashes for OPC replacement

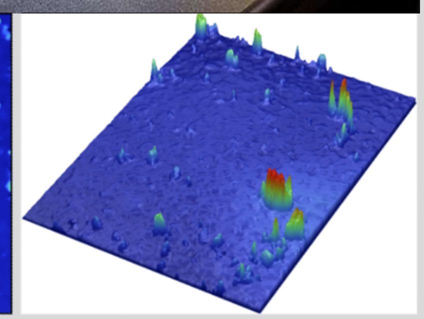


Back-to-the-basics: Fly ash dissolution rates using vertical scanning interferometry (VSI)

- Combination of optical and interference microscopy
- Lateral resolution limited by optics, here around 200 nm
- Z-resolution, determined by ability to track interference fringes (beam split) ≈ 0.1 nm
- NewView 8200 optical profiler fitted with multiple objectives
- Typical image field: 1000s of μm^2 and can be further expanded

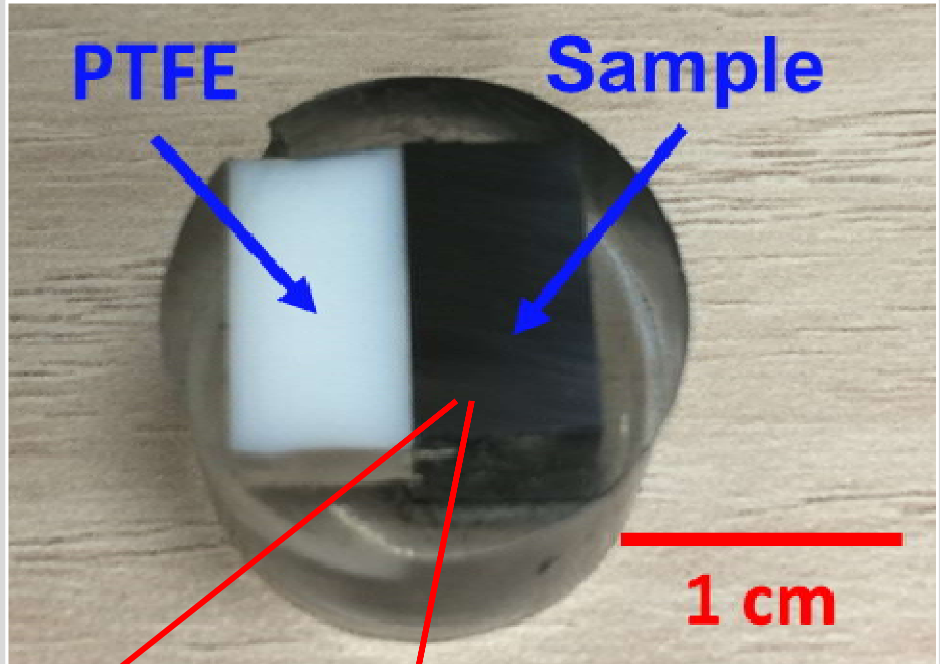


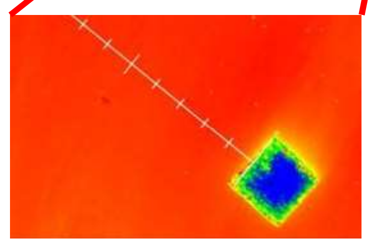




Interferometric Imaging strategy

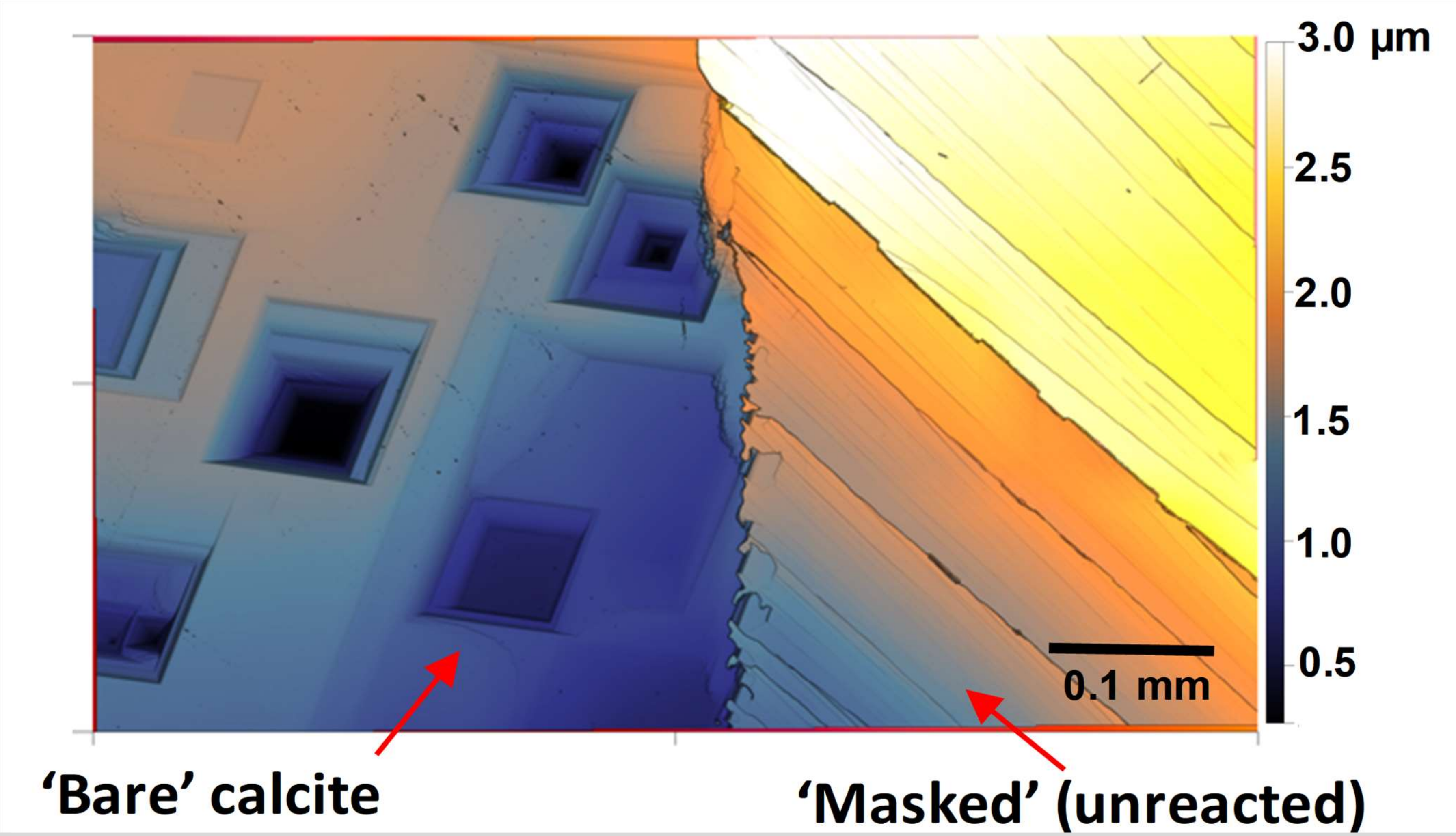
- Two adjacent surfaces:
  - Sample surface (changes in time)
  - PTFE reference (quartz is another)
- Compare surfaces to each other. This allows for absolute height analysis (S_a = 29 ± 8.7 nm)
- It is critical to have an “inert” reference as due to imaging resolution, small changes (10s of nanometers) can completely change the results
- PTFE is noted to be truly inert





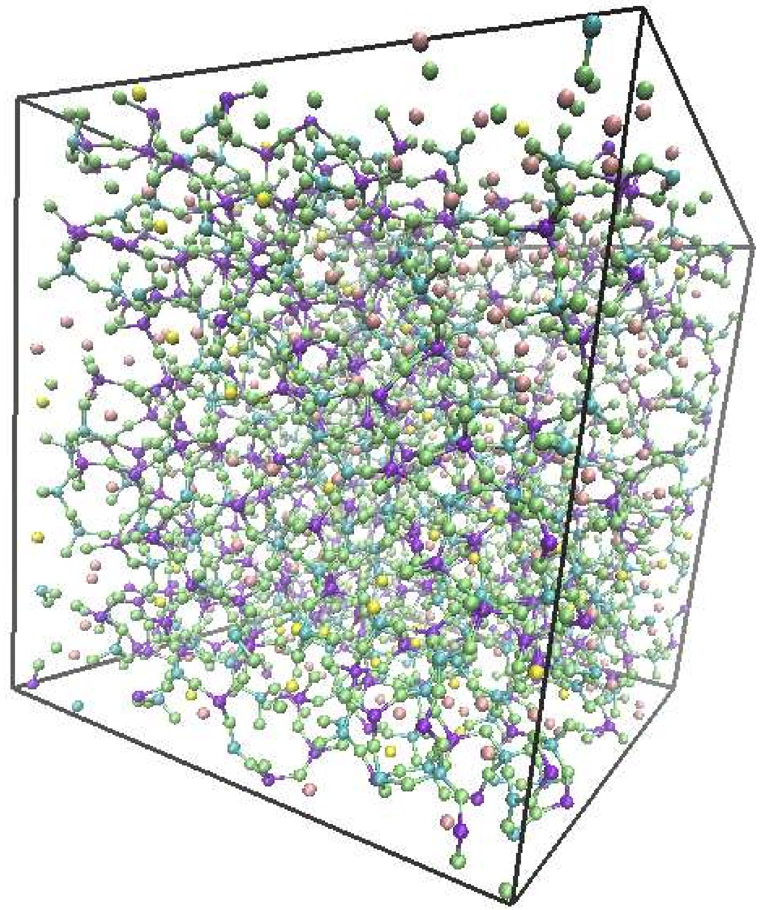
“Fiducial mark” to re-orient and re-align the images

Quantifying reactions (at surfaces and interfaces)

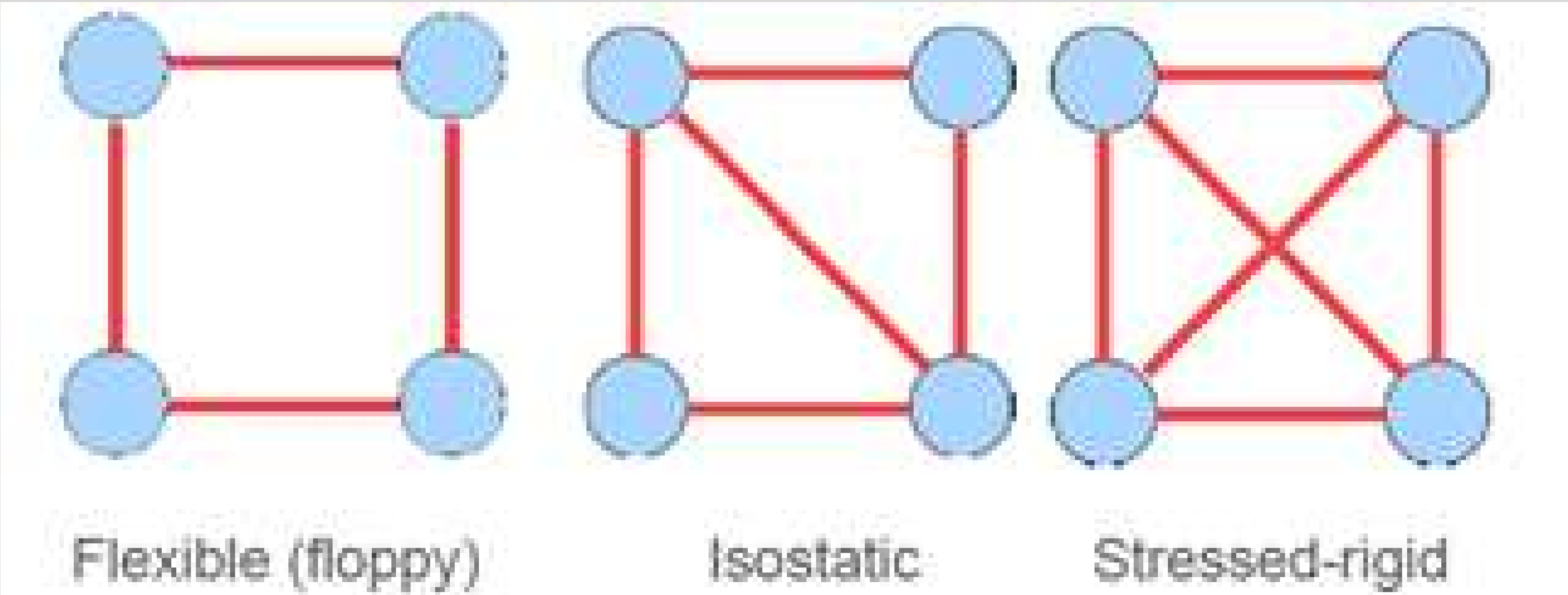


A molecular-scale view into the structure of (aluminosilicate) glasses

- Construct the atomic structure
- For a crystal; straightforward using known atomic positions
- For a glass insert "atoms in a box" based on composition. Heat the system (4000 K) and rapidly cool it (1 K/ps) and relax the structure
- Carried out in LAMMPS using classical or semi-classical interatomic potentials

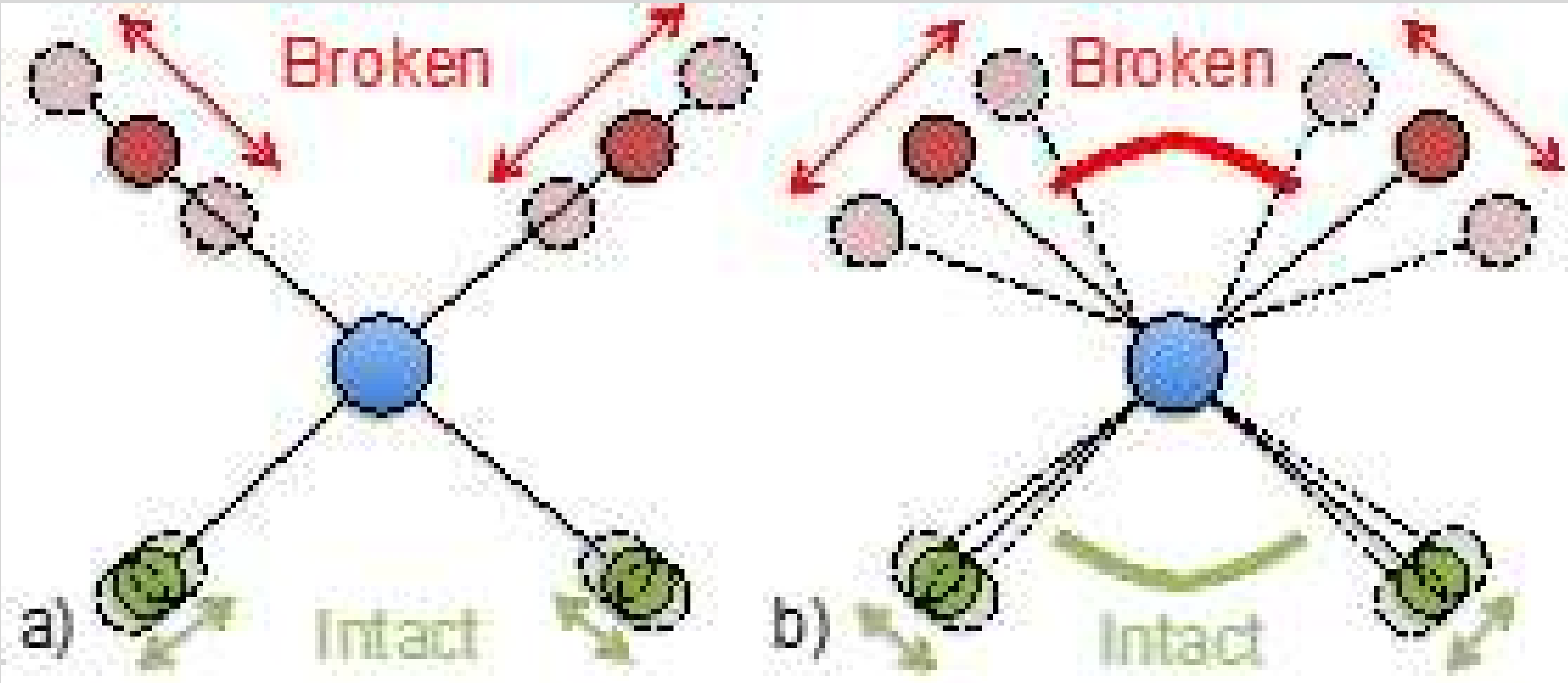


Analysis of the atomic network's rigidity



- **Mechanical truss: slender, but rigid members which link together at joints**
  - **Simple analogy: joints = atoms, and slender members = atomic bonds**
- **Several options: determinate ($m = 2j-r$), indeterminate ($m+r > 2j$), unstable …**

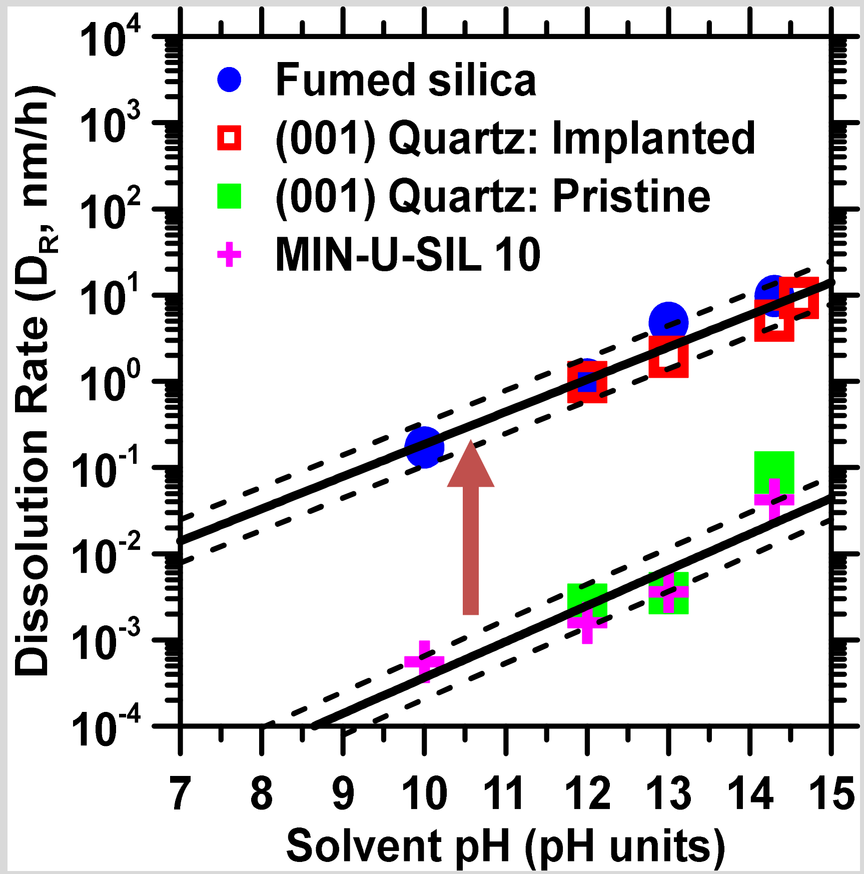
Analysis of the atomic network's rigidity



- For a central atom, determine the number of permissible BS and BB constraints by assessing the radial and angular excursions, of each neighboring atom (MD simulations)
- Low (or high) radial/angular excursions are associated with intact (or broken) constraints

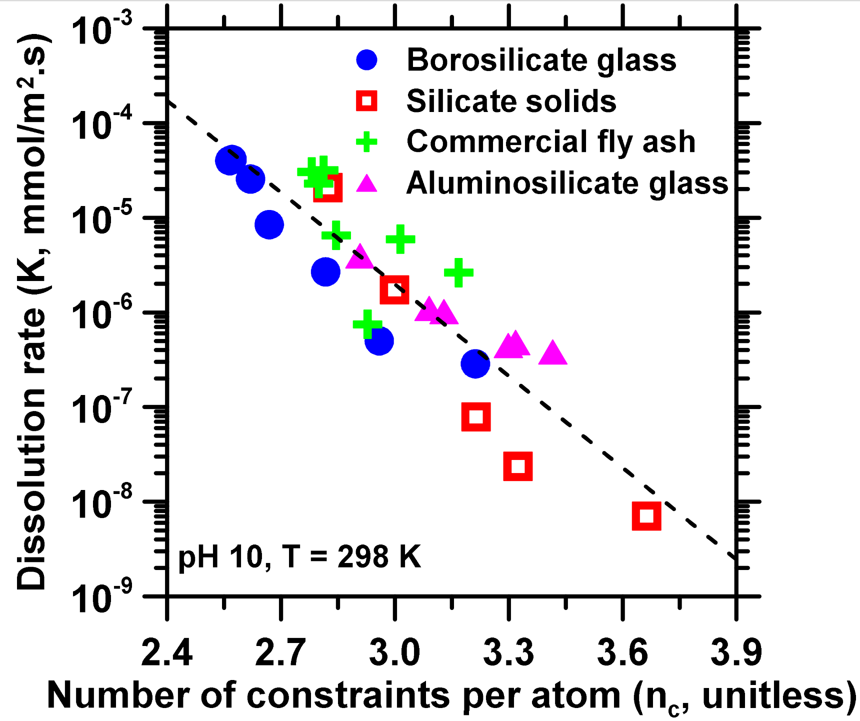
Consider the (simple) case of silica and quartz

- Of course, it is well-know that silica dissolves faster than quartz
- But the explanation of why so is qualitative" – "poor-order or lack of crystal structure" in silica
- **Quartz:** dissolution rate increases 3 orders of magnitude following its irradiation – this has obvious impacts on durability
- How this links atomic topology and changes in it, to reactivity ?



Network rigidity as an indicator of reactivity

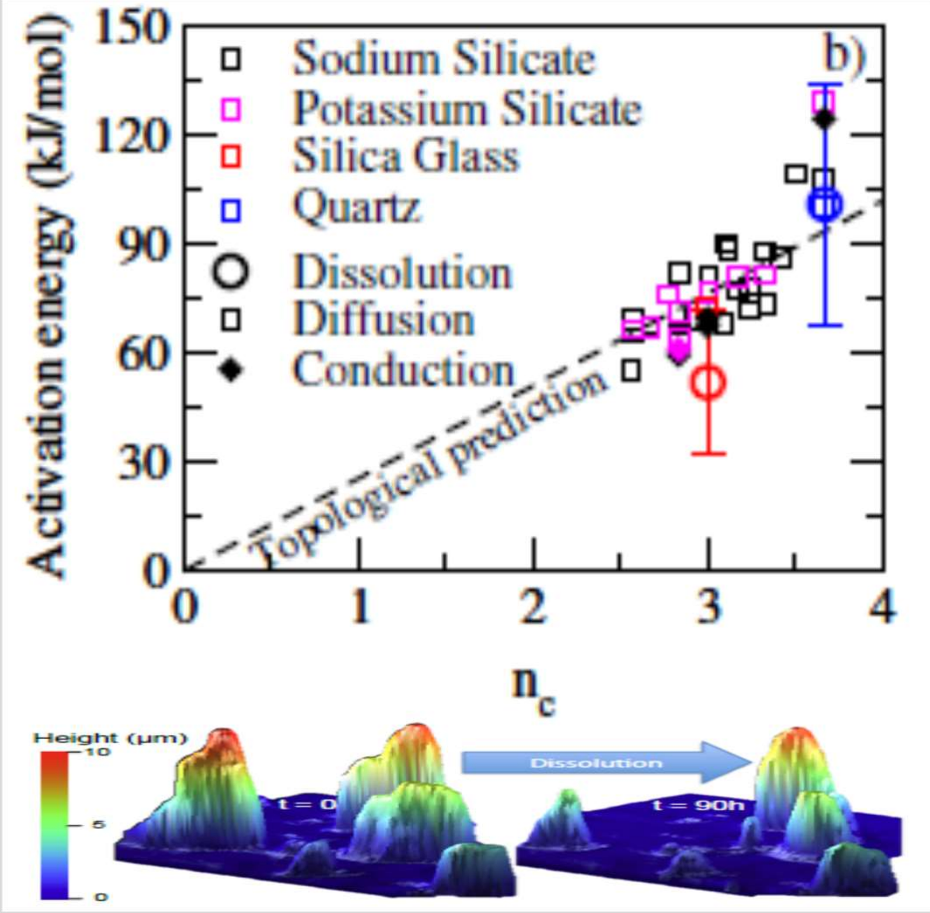
- The number of constraints is an effective indicator of solid's reactivity – i.e., of tendency for framework dissolution/rupture
- The energy required to break a unit constraint is controlling feature that relates to other transport controlled processes, e.g., diffusion, dissolution and conduction since $E_A = n_c E_0$, reveals the activation energy



$r_{diss} = K_0 \exp[n_c E_0/RT]$: *Arrhenius like relation*
where: $K_0 = 2.6 \times 10^{10}$ µmol/(m².s)
$E_0 \approx 25$ kJ/mole (i.e., the energy needed to rupture a single atomic constraint)

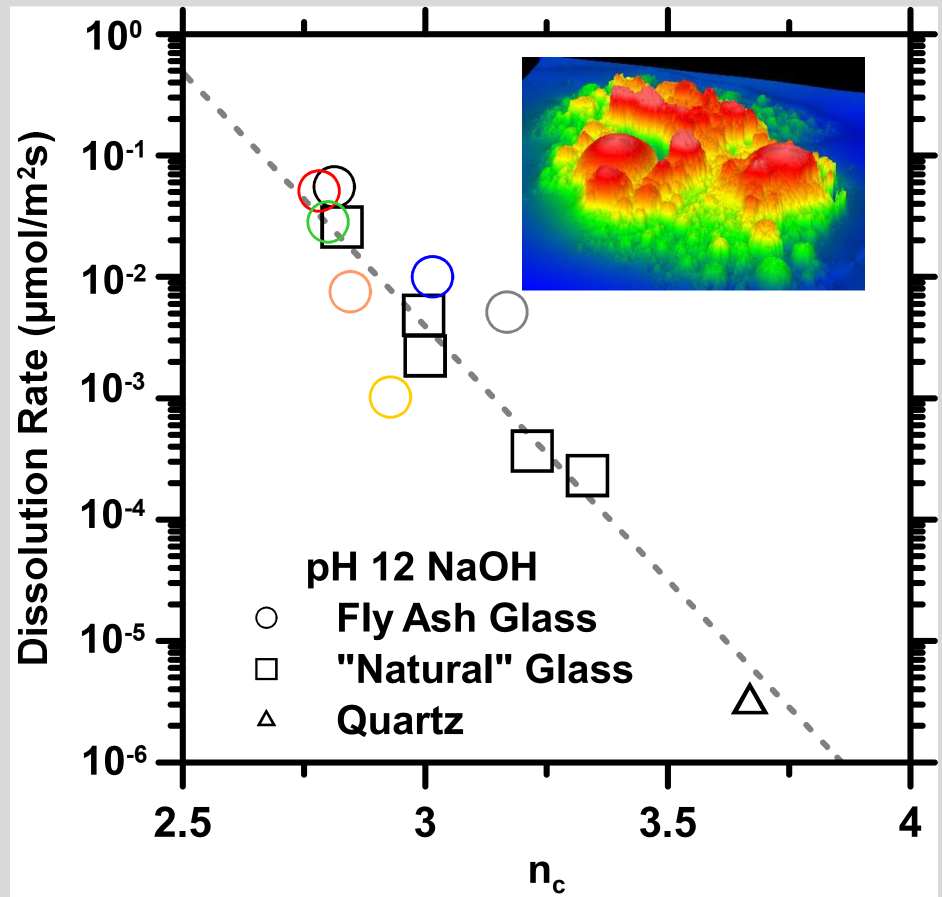
Dissolution, diffusion and conduction have a common "topological origin" … ?

- Once again, consider: $E_A = n_c E_0$
- If we compare the activation energy of self-diffusion (Na, K), conduction (Na, K) and dissolution (quartz, silica) it appears these processes have a common "topological origin"
- This suggests that each of the processes have a common energy barrier: the rigidity of the atomic network



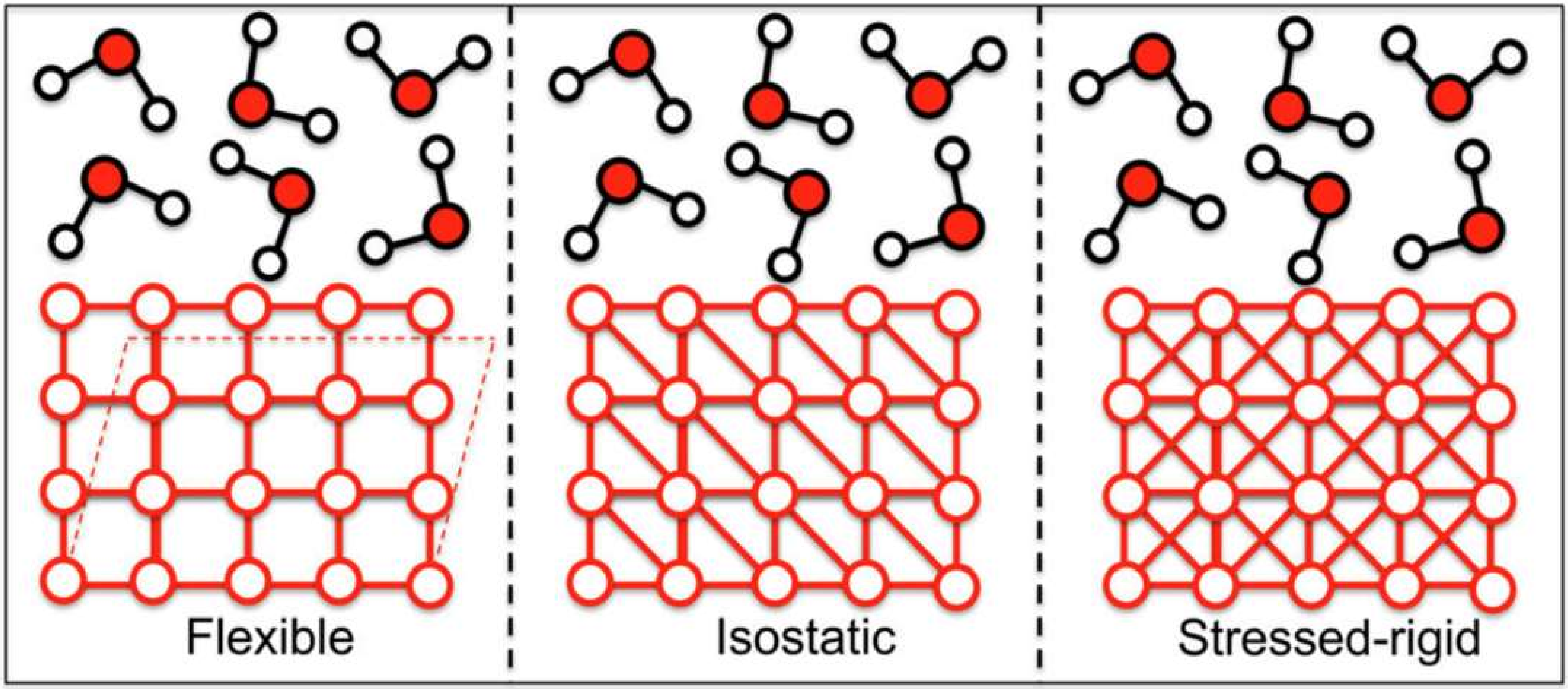
Linking network rigidity (glass connectedness) to chemical reactivity of fly ashes

- The dissolution rates of the glass components of fly ashes follow "topological scaling" relation (wherein: Nr α n_c)
- Indeed, fly ash data coincides with that of fully compensated glasses, and natural minerals
- The E_0 value is slightly reduced due to presence of modifiers, but rupture energy is controlled by $[SiO_4]^{4-}$ and/or $[AlO_4]^{5-}$ units



$r_{diss} = K_0 \exp[n_c E_0/RT]$: $E_0 \approx 24$ kJ/mole

So why do disordered solids dissolve faster?: An explanation based on atomic topology



n_c = 2.770 (flexible) | **n_c = 3.000** | **n_c = 3.077 (rigid)**

Summary and outcomes

- We have developed a wide range of tools, methods and protocols to establish composition-chemical reactivity-engineering performance relations for fly ashes
- A pioneering combination of vertical scanning interferometry (VSI) and MD simulations has elucidated a “topological framework” which rationalizes the differing composition/structure dependent reactivities of a range of silicates, including minerals and fly ashes
- This framework with relevant enhancements is readily applicable to assess and rank WTE-ashes for applications such as cement (OPC) replacement in concrete